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Multifunctional Composites through Inkjet-printed Architectures

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14. ABSTRACT This project report builds upon the previously reported results obtained from the pioneering project funded by EOARD (FA8655-11-1-3072), in which, for the first time, an inkjet printer was successfully used to prepare self-ameliorating composite systems for aircraft structures [1-3]. A range of polymer systems were printed onto carbon fibre composite pre-preg using the same consistent hexagonal pattern. After curing, the composite systems were optimised and tested to determine their fracture toughness and shear properties. Self-repairability of 30-40% has been obtained from 0.02% microscopically accurate addition of jetted polymer agent between the composite plies, prior to the cure process. Inkjet printing is a flexible method to print patterns that can be designed before printing, and this technique can be used to selectively toughen composite areas where higher damage resistance is required, such as holes, joints and other stress concentration areas. In this work, PMMA micro-droplets were printed onto prepreg before curing, and remained arrested between composite plies without direct contact with the neighboring micro-droplets after curing, which preserved the structural integrity of the novel composite system. As the thickness of deposits on substrate by inkjet printing is sub-micron, the introduced thickness to the composite is negligible, which is an advantage over conventional toughening methods. Since the interface between the plies is likely to be the main source of micro-cracks, discrete thermoplastic microdroplet deposition imparts multifunctional properties whilst enhancing its structural integrity in service.					
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Multifunctional Composites through Inkjet-printed Architectures

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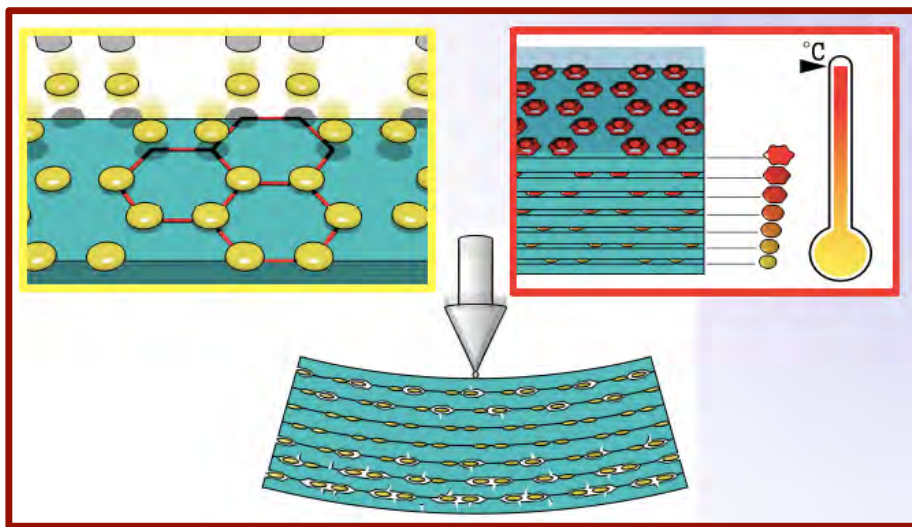


Illustration: Inkjet printed PMMA deposited between composite layers, heated during the cure cycle and exposed to damage prior to self-reconfigurable heat treatment.

Table of Contents

1. Summary
2. Methods and Procedures
 - 2.1 Materials
 - 2.2 Fabrication of Specimens
 - 2.3 Experimental Work
3. Results and Discussion
 - 3.1 Fracture Toughness
 - 3.2 Inspection of individual droplets
4. Fractographic analysis of DCB tested samples
5. Conclusions
6. Acknowledgements
7. References

List of Figures

Figure 1. G_{Ic} comparison of different printing layers of PMMA deposited between CFRP unidirectional plies.

Figure 2. Schematic representations of four different patterns used in this work.

Figure 3. G_{Ic} comparison of different printing patterns deposited between CFRP unidirectional plies.

Figure 4. Optical images of epoxy coated glass substrates with printed PMMA deposits (hexagon, $dx/dy = 0.4/0.2$ mm). a), c) and e) 5, 10, and 20wt% PMMA deposits before heating cycle; b), d) and f) 5, 10 and 20wt% PMMA deposits after heating cycle.

Figure 5. Reduction in PMMA droplet diameter after the heating cycle.

Figure 6. Optical images of epoxy coated glass slides with printed 10 wt.% PMMA deposits twice before (a) and after (b) heating cycle.

Figure 7. Optical images of epoxy coated glass substrates with printed PMMA lines before (a) and after (b) heating.

Figure 8. Optical images of epoxy coated glass slides with printed PMMA continuous thin film before (a) and after (b) heating.

Figure 9. G_{Ic} comparison of specimens with printed thin film and discrete dots pattern [3].

Figure 10. SEM images of fracture surfaces of DCB tested samples with PMMA depositions.

Figure 11. SEM images of fracture surfaces of DCB tested samples with printed PMMA thin film.

List of Tables

Table 1. DCB test results of samples printed with different layers of PMMA inks using the same printing pattern.

Table 2. DCB test results of samples with printing different PMMA patterns.

Table 3. Diameters of PMMA depositions/beads before and after heating cycle.

1. Summary

This project report builds upon the previously reported results obtained from the pioneering project funded by EOARD (FA8655-11-1-3072), in which, for the first time, an inkjet printer was successfully used to prepare self-ameliorating composite systems for aircraft structures [1-3]. A range of polymer systems were printed onto carbon fibre composite pre-preg using the same consistent hexagonal pattern. After curing, the composite systems were optimised and tested to determine their fracture toughness and shear properties. Self-repairability of 30-40% has been obtained from 0.02% microscopically accurate addition of jetted polymer agent between the composite plies, prior to the cure process. Inkjet printing is a flexible method to print patterns that can be designed before printing, and this technique can be used to selectively toughen composite areas where higher damage resistance is required, such as holes, joints and other stress concentration areas.

In this work, PMMA micro-droplets were printed onto prepreg before curing, and remained arrested between composite plies without direct contact with the neighbouring micro-droplets after curing, which preserved the structural integrity of the novel composite system. As the thickness of deposits on substrate by inkjet printing is sub-micron, the introduced thickness to the composite is negligible, which is an advantage over conventional toughening methods. Since the interface between the plies is likely to be the main source of micro-cracks, discrete thermoplastic microdroplet deposition imparts multifunctional properties whilst enhancing its structural integrity in service.

2. Methods and Procedures

2.1 Materials

An aerospace grade unidirectional carbon fibre prepreg (Cycom 977-2, Cytec Industries Inc., USA) was chosen as substrate in this work. Poly(methyl methacrylate) (PMMA) ($M_n = 15$ kDa) was dissolved in N, N-dimethylformamide (DMF) with different concentrations. All chemicals were purchased from Sigma Aldrich (Sigma-Aldrich Co. Ltd., UK) and used as received. As aforementioned, the viscosity of ink is an important parameter for inkjet printing, hence viscosities of all inks used in this work were measured at room temperature using an A&D sine-wave vibro viscometer (European Instruments, UK).

2.2 Fabrication of specimens

A drop-on-demand (DOD) JetLab 4xl printer equipped with a compatible MicroJet printhead was used to print the prepregs before the curing cycle. The diameter of printhead orifice was 60 μm , all printing devices were purchased from MicroFab Inc. (Plano, USA). Prepreg sheets were cut into 150×140 mm and 100×100 mm for DCB test and impact test respectively. For DCB test, only the mid-thickness ply was printed with PMMA solution. For impact test, PMMA was deposited between all the plies. Parameters dx and dy can be verified to change shape and density of patterns [3]. After printing, the plies were laid-up unidirectionally in accordance with the test standard BS ISO 15024:2001. A non-adhesive polytetrafluoroethylene (PTFE) film was inserted at the mid-thickness of the panel during lay-up to simulate a sharp starter crack. Autoclave (Premier Autoclaves Ltd., UK) was used to cure panels. For the detailed curing cycles please refer to our previous work [1]. DCB test specimens were cut from cured laminates with the required dimensions as described in the standard.

2.3 Experimental work

DCB test was adopted to measure the Mode I interlaminar fracture toughness (G_{Ic}). The DCB test was carried out using a tensometer equipped with a 500 N load cell (TA500 Texture Analyser, Lloy Instruments, UK) with a crosshead speed of 5 mm/min. A mode I pre-loading was carried out to avoid resin rich regions and to generate a real crack for the subsequent DCB test.

Optical microscopy was extensively used to identify the microscopic changes in the printed systems before and after the curing cycle, and also after the reheating of the system to mimic the self-reconfigurable process in heat assisted environment.

3. Results and Discussions

3.1. Fracture toughness

Figure 1 shows the G_{Ic} comparison of samples with different printing layers using the same printing pattern (PMMA, rectangle, $dx/dy = 0.4/0.2$ mm). As expected, the G_{Ic} of samples with PMMA deposits were higher than that of NP group. Theoretically, the group with printed two 10 wt.% PMMA layers of pattern should have the same amount of PMMA deposition as the group with printed one 20 wt.% PMMA layer using the same pattern. And the results agreed with the expectation that increase of G_{Ic} of these two groups are about the same as shown in Table 1. However, the twice amount of PMMA usage did not give a corresponding toughening efficiency.

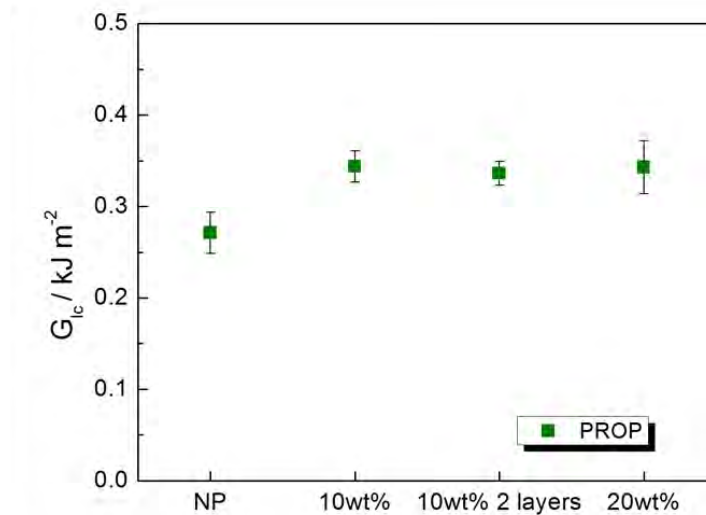


Figure 1. G_{Ic} comparison of different printing layers of PMMA deposited between CFRP unidirectional plies.

Since the concentration of PMMA has an effect on the G_{Ic} of final composites, it is worthwhile to investigate the difference between the systems with discretely deposited microscopic patterns, and that with the fully printed surface. Firstly, 10 wt.% PMMA was used to print four different patterns while keep the same material usage per unit area. Figure 2 schematically shows these four different patterns with their respective dimensions.

Table 1. DCB test results of samples printed with different layers of PMMA inks using the same printing pattern.

Group	$G_{Ic} / \text{kJ m}^{-2}$			Increase / %
	NL	5% / MAX	PROP	
NP	0.275	0.288	0.271	—
10 wt. %	0.316	0.351	0.344	15 ~ 27%
10 wt. % 2 layers	0.327	0.357	0.336	19 ~ 24%
20 wt. %	0.328	0.337	0.343	19 ~ 27%

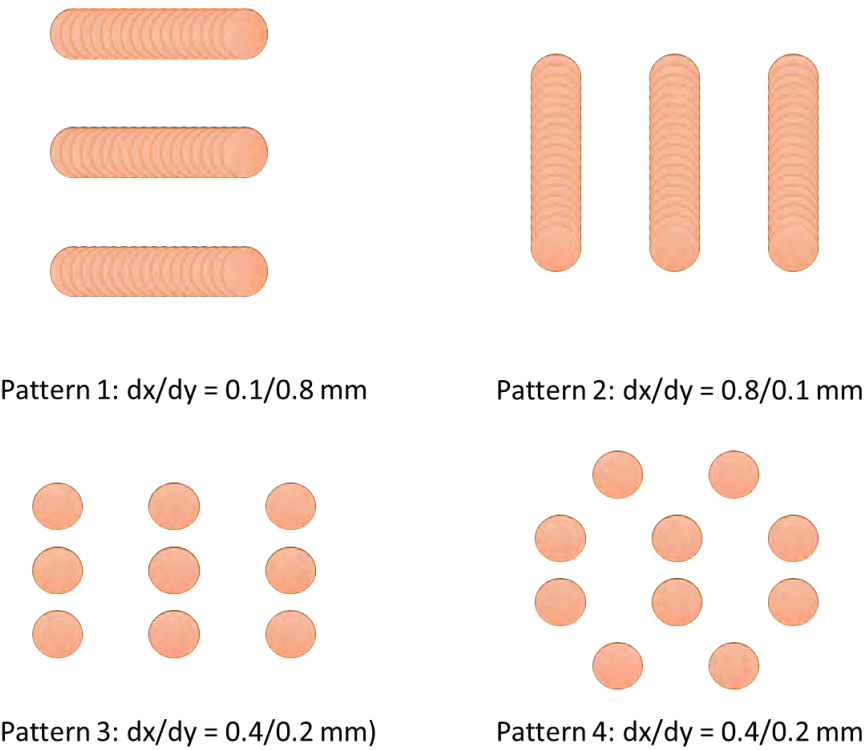


Figure 2. Schematic representations of four different patterns used in this work.

The four groups with printed PMMA patters improved G_{Ic} as expected, where the groups with discrete printed patterns produced higher G_{Ic} . Table 2 shows the results of these tests.

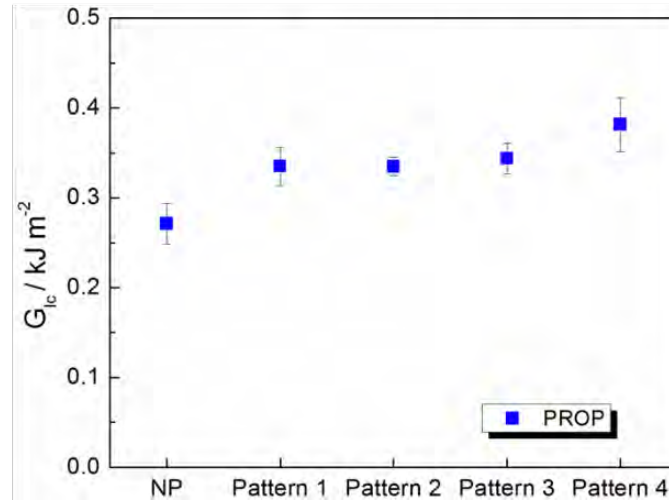


Figure 3. G_{Ic} comparison of different printing patterns deposited between CFRP unidirectional plies.

Table 2. DCB test results of samples with printing different PMMA patterns.

Groups	$G_{Ic} / \text{kJ m}^{-2}$			Increase / %
	NL	5%/MAX	PROP	
NP	0.275	0.288	0.271	—
Pattern 1	0.319	0.355	0.335	16 ~ 24%
Pattern 2	0.314	0.342	0.334	14 ~ 23%
Pattern 3	0.316	0.351	0.344	25 ~ 27%
Pattern 4	0.355	0.392	0.382	29 ~ 41%

3.2. Inspection of individual droplets

In order to find out the damage mechanism of the G_{Ic} improved CFRP laminates, it is of interest to know the behaviours of polymer depositions between laminate plies before and after curing. Unfortunately, the black background and fibrous texture of CFRP make the observation of printed polymer deposition between laminate plies extremely difficult. Therefore, glass substrates were coated with a thin layer of epoxy resin to mimic the matrix of prepreg as the potential behaviours of polymer depositions are mainly involved with the epoxy resin.

Three different PMMA concentrations (5, 10 and 20 wt.%) were used to print a uniform hexagonal pattern. Figure 4 shows the optical microscope images of patterns printed on epoxy coated glass substrates before and after heating cycle with the pressure provided equivalent to the autoclave curing cycle conditions. The printed PMMA depositions tended to form spherical particles while keeping the positions in hexagon pattern after the heating cycle.

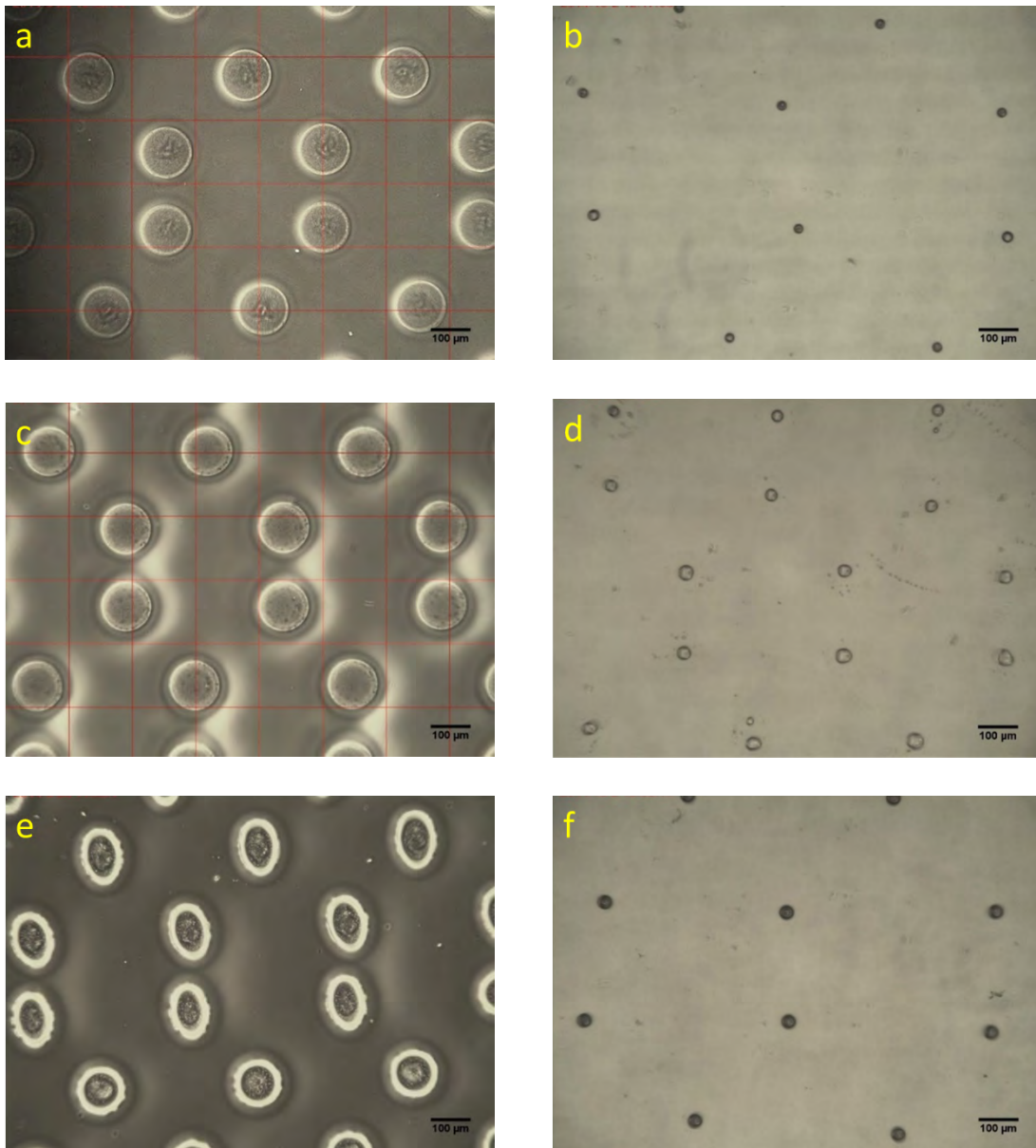


Figure 4. Optical images of epoxy coated glass substrates with printed PMMA deposits (hexagon, $dx/dy = 0.4/0.2$ mm). a), c) and e) 5, 10, and 20wt% PMMA deposits before the heating cycle; b), d) and f) 5, 10 and 20wt% PMMA deposits after the heating cycle.

The diameters of PMMA depositions printed on the epoxy coated glass substrates of three solutions with different PMMA concentrations were quite similar before heating. However, the diameters of PMMA beads varied depending on the polymer concentration after heating. As it shown in Figure 5, the diameter of PMMA beads increases as the PMMA concentration/amount increases after heating, therefore, the percentage of decrease in diameter of depositions decreases as the PMMA concentration/amount increases.

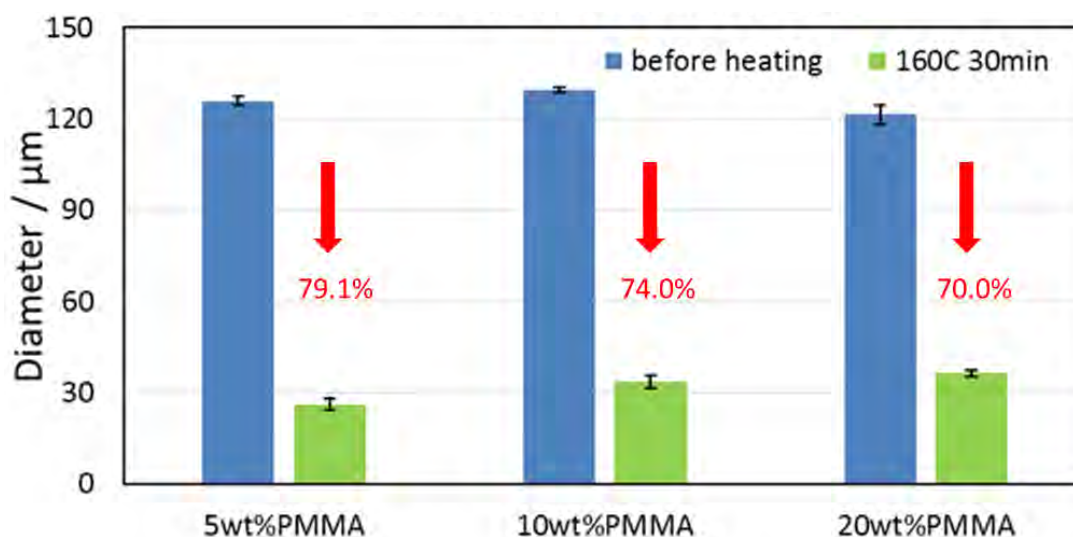


Figure 5. Reduction in PMMA droplet diameter after the heating cycle.

In order to verify that the % of polymer concentration influenced the diameter of PMMA droplets after heating, multilayer printing was conducted to increase the amount of PMMA by increasing the number of printed layers instead of using a high concentration PMMA. Figure 6 shows the printed pattern before and after heating cycle.

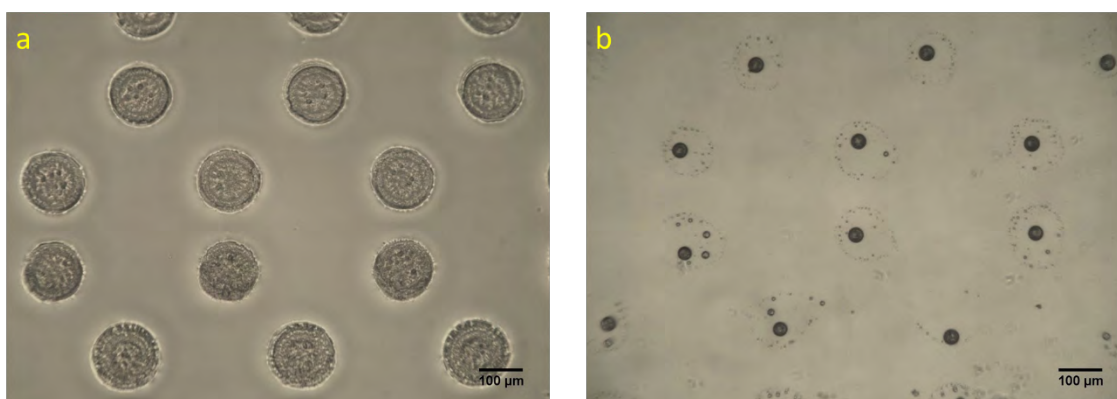


Figure 6. Optical images of epoxy coated glass slides with printed 10 wt.% PMMA deposits twice before (a) and after (b) the heating cycle.

A 10 wt.% PMMA was used to print the hexagonal pattern ($dx/dy = 0.4/0.2$ mm) twice, and the diameter of PMMA deposition after the repeated printing process may have been slightly larger than that of single printing process before the heating. In terms of the diameter of PMMA beads, theoretically, the diameter of PMMA droplet using 10 wt.% PMMA should be equal to that of PMMA beads using 20 wt.% PMMA. The results highly agreed with the theoretical prediction. Table 3 shows the results of this comparison.

Table 3. Diameters of PMMA depositions before and after the heating cycle.

Ink	Before heating / μm	STDEV	After heating / μm	STDEV
10 wt.%	129.5	1.0	33.7	2.1
10 wt.% twice	147.4	3.3	36.8	2.0
20 wt.%	121.4	3.1	36.4	1.1
Note: STDEV represents standard deviation, $n = 10$				

Further, 10 wt.% PMMA was used to print line patterns to inspect possible changes after the curing cycle. Figure 7 shows the printed lines before and after heating. It can be seen that the continuous lines broke down to uneven sized droplets, again indicating the capability of PMMA to reconfigure its structure within this system after the thermal cycle.

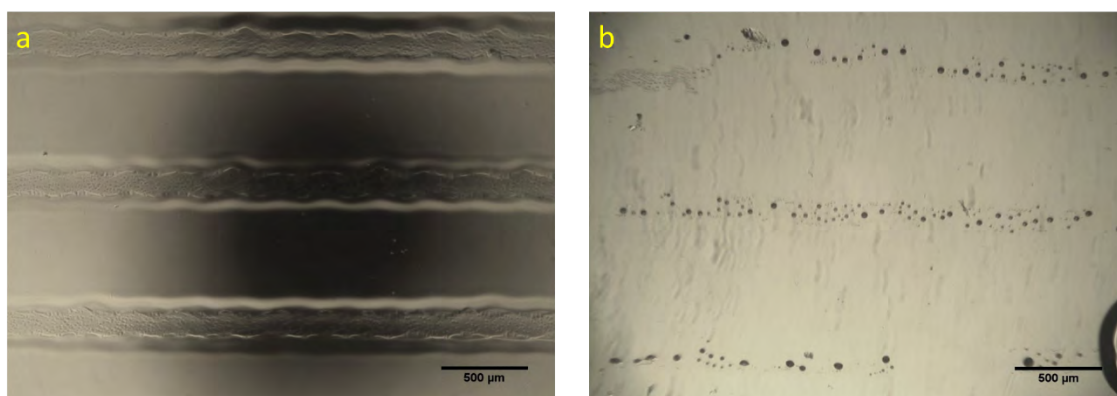


Figure 7. Optical images of epoxy coated glass substrates with printed PMMA lines before (a) and after (b) heating.

Finally, a thin film of PMMA was printed onto the epoxy-coated glass substrate. Figure 8 shows the printed PMMA thin film before and after heating. It can be seen that the continuous thin film broke down to randomly distributed droplets with a wide range of diameters. This phenomenon could be used to explain the unstable crack growth of samples with printed PMMA thin film in DCB tests.

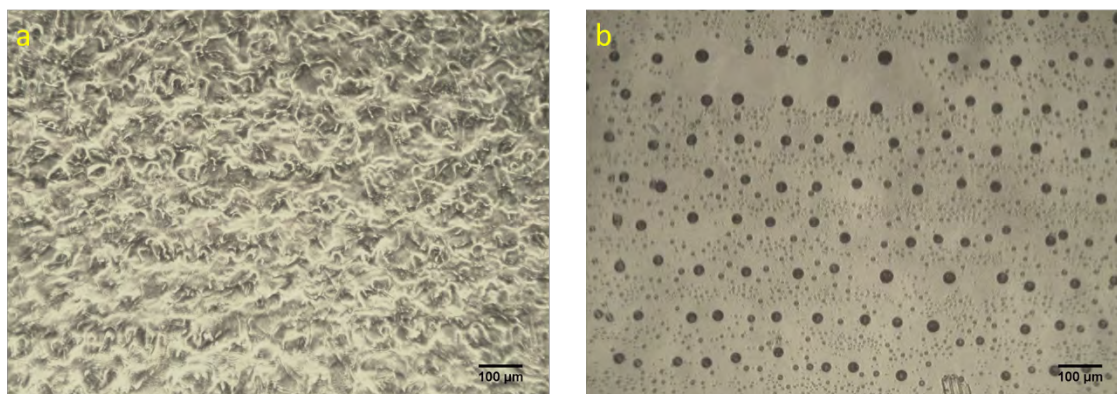


Figure 8. Optical images of epoxy coated glass slides with printed PMMA continuous thin film before (a) and after (b) heating.

4. Fractographic analysis of DCB tested samples

SEM was used to analyse the fracture surfaces of polymer printed CFRP samples after DCB tests. More information about the DCB results can be found in our earlier publications [1-3]. The most representative set of results relevant to this report is shown in Figure 9, showing the distinct improvement in the predictability of the results for discretely printed patterns. It should be noted that 10%wt PMMA film is relatively comparable with 20%wt PMMA dots due to the same volume fraction of PMMA. Although the fracture toughness of PMMA film deposition CFRP system is increased, so is the standard deviation and the irregular crack propagation, which seems to be well arrested by the discretely printed system.

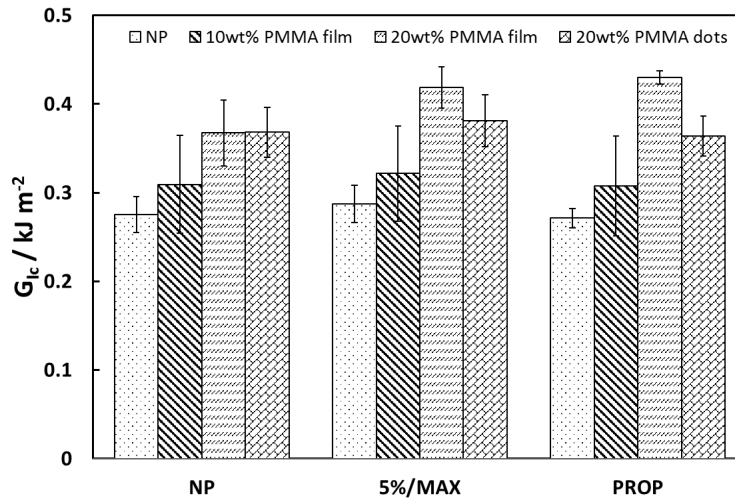


Figure 9. G_{Ic} comparison of specimens with printed thin film and discrete patterns [3].

When PMMA droplets were printed between laminate plies, spherical PMMA beads formed a second phase as shown in Figures 9 and 10. Due to the complex texture of CFRP laminate, and the severe damage along the test surface, the discrete dot-patterns were hardly identified, however the scattered droplets can be observed as shown in Figure 10(a) and (b). The fracture surfaces of samples with printed PMMA thin film agreed with the observation of epoxy coated glass substrates. The printed film increased the ductility of the fracture surface as shown in Figure 11.

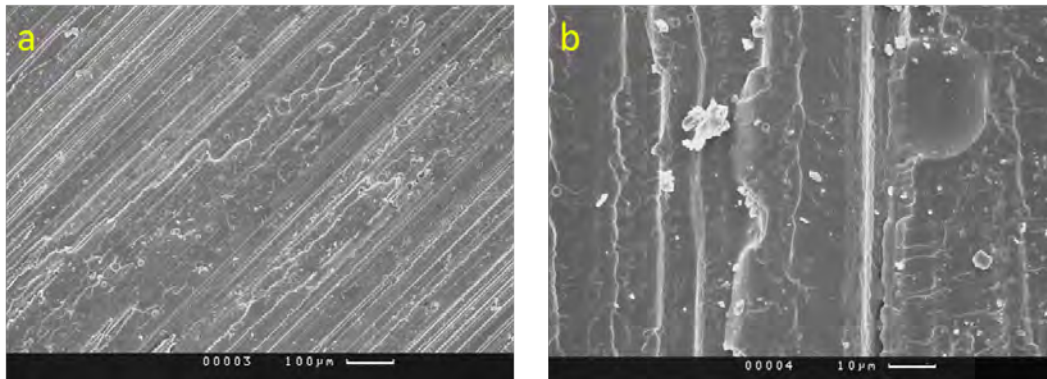


Figure 10. SEM images of fracture surfaces of DCB tested samples with PMMA depositions.

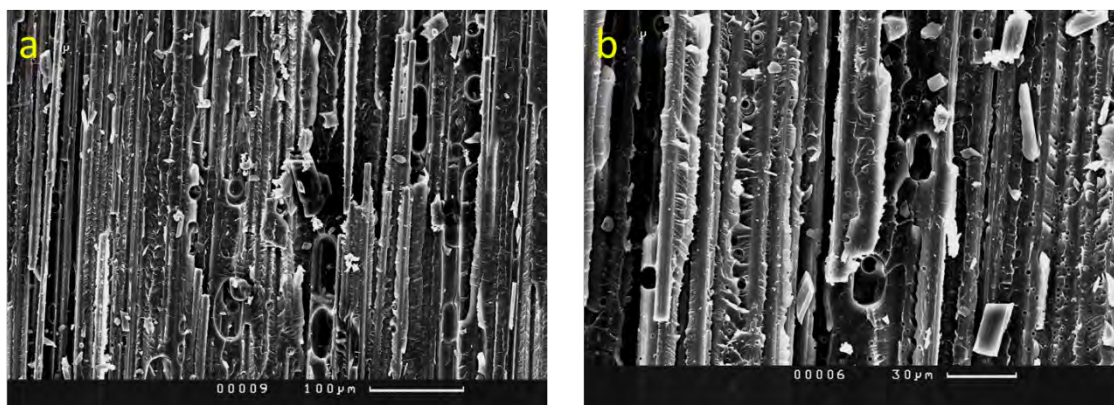


Figure 11. SEM images of fracture surfaces of DCB tested samples with printed PMMA thin film.

5. Conclusion

The mechanism by which addition of thermoplastic droplets toughens a composite material has not been well understood before this study. We proposed the following explanations before commencing this project: (1) PMMA beads act as plastic zones that can absorb energy by plastic deformation. Due to the viscoelastic nature of PMMA, those well dispersed microphases by inkjet printing provide an energy-absorption path by thermoplastic deformation, which can decelerate crack growth as the crack tips are shielded by those plastic zones. (2) Crack propagation is arrested by the combination of crack-diverting discretely deposited droplets and the higher fracture toughness of PMMA. The second option can be further evidenced by the lower standard deviation in the system with hexagonally printed 20% PMMA system. The future work will be conducted using x-ray tomography in-situ during the 4-point bend test experiments before and after the heating cycles, to validate the results from this study.

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2. Yi Zhang, Jonathan Stringer, Richard Grainger, Patrick J Smith and Alma Hodzic, Fabrication of patterned thermoplastic microphases between composite plies by inkjet printing, *Journal of Composite Materials*, published online 8 May 2014, DOI:10.1177/0021998314533715.
3. Y. Zhang, J. Stringer, P.J. Smith, A. Hodzic and R. Grainger, Toughening composites with self-ameliorating capability using inkjet printing technique, ECCM16 - 16TH European Conference On Composite Materials, Seville, Spain, 22-26 June 2014.